(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 102 414**
A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **82304050.6**

(22) Date of filing: **30.07.82**

(51) Int. Cl.³: **A 43 B 23/16**
B 32 B 27/12

(43) Date of publication of application:
14.03.84 Bulletin 84/11

(84) Designated Contracting States:
DE GB IT

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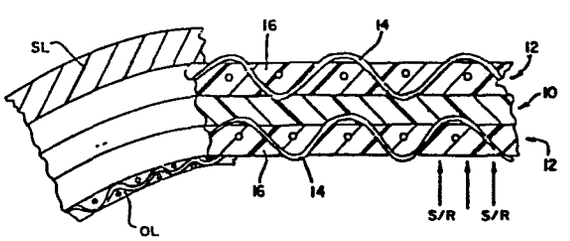
(54) Reinforcing laminate.

(57) A reinforcing laminate 10,12 comprising a core layer 10 of thermoplastic resin and strength layers 12 of fabric saturated with a styrene saturant is first produced, the saturant being a solvent- or heat-activatable adhesive and the fibres of the fabric being locked into the resin layer. The laminate 10,12 is mouldable into complex, compound curved shapes and preferably simultaneously bondable to substrate and cover layers SL,OL to provide a tough, water resistant reinforcement usable in outdoor or military boots.



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REINFORCING LAMINATE

DESCRIPTION

The present invention relates to reinforcing laminates, particularly in connection with reinforcing elements for shoes and more particularly military and outdoorsmen's boots subject to rugged long-term use, water, oil and weather exposure.

In such boot or related application, the use of external adhesives is undesirable because (a) long-term usage tends to degrade such external adhesives, (b) slow, costly processing is entailed with latex adhesives, (c) critical time/temperature/pressure relationships during manufacture are often required, and (d) residual thermosensitivity of hot melt adhesives is a further handicap. The requirement is not completely met by ionic resin stiffening elements as described in U.S. Patent No. 3 427 733 to Beckwith. Older more traditional materials such as the polyethylene reinforced fabric of U.S. Patent No. 2 734 289 to Heaton et al., as well as cardboard or rubber, have also proven inadequate.

The present invention provides a laminate comprising at least one layer of thermoplastic resin and at least one solvent- or heat-activatable adhesive impregnated cloth layer, the layers being bonded to each other at least in part through locking of cloth fibre portions of the cloth layer into the adjacent resin layer and the adhesive impregnant comprising a styrene saturant which

is capable of impregnation into the cloth layer in liquid form and hardenable therein to form a stiff solid layer.

The invention also provides a process of making a laminate, the process comprising extruding a thermoplastic resin to form a resin layer, adhering a cloth layer to the freshly-extruded resin layer and impregnating the cloth layer with a solvent- or heat-activatable adhesive comprising a styrene saturant which is capable of impregnation into the cloth layer in liquid form and hardenable therein to form a stiff layer.

The saturant may comprise styrene or a mixture of styrene and one or more copolymerisable monomers.

The present invention can thus provide a mouldable, stiff reinforcing laminate which can be water, oil, impact and weather resistant. The laminate can be self-adhering to a carrier surface or substrate and/or cover layer to be reinforced by the adhered layer. The laminate may be produced at a high rate and utilizing inexpensive components and materials.

In accordance with the invention, cloth is laminated with a thermoplastic resin layer and then saturated with a solvent- or heat-activatable adhesive and stiffening material, preferably styrene which is activatable by aromatic solvents or through heat activation. Preferably two such fabric layers are bonded to a freshly extruded resin layer to sandwich it as drawn from an extruder. The preliminary laminate thus formed is then caused to be saturated in its fabric layer(s) with a solvent- or heat-activatable adhesive impregnant to produce a final laminate. The final laminate thus formed can be shipped in rolls and spread and cut to desired forms by users for moulding and adhesively bonding to a supporting substrate and (optionally) overlapping with a cover or liner, also by adhesive bonding. The adhesion can be afforded by

preliminary solvent- or heat-activating (preferably solvent-activating) at least one of the impregnant layers prior to pressure and heat activation of the laminate in the course of moulding.

The fabric provides exposed fibrous ends which can adequately bond to freshly extruded core resin and penetrate therewithin for geometric locking between the fabric and such core resin to adhere the fabric layer to the resin before and after impregnating the fabric.

Preferably the resin layer is an ionic copolymer of a monomer feed comprising at least 50 mole percent of an α-olefin having the general formula RCH = CH_2 where R is selected from the class consisting of hydrogen and 1 to 8 carbon atom alkyl radicals, 0.12 to 25 mole percent of an α,β-ethylenically unsaturated mono-carboxylic acid and 0.2 to 25 mole percent of an α,β-ethylenically unsaturated di-carboxylic acid, the copolymers having at least a uniformly distributed 10 percent of the carboxylic acid groups of the mono- and di-carboxylic acids therein neutralized by metal ions of 1 to 3 valence.

The tough resin layer may also be a thermoplastic hydrocarbon resin derived from olefin monomer described in U.S. Patent No. 3 427 733 of February 18, 1979 to Beckwith describing a laminate of such resin with fabric affording advantages in a stiffening element. Such material, an "ionomeric resin" incorporating therein ionic bonds in a thermoplastic polymer resin, may be more fully described as an ionic copolymer selected from the class consisting of polymers of α-olefins having the general formula RCH =CH_2 where R is a radical selected from the class consisting of hydrogen and alkyl radicals having from 1 to 8 carbon atoms, the olefin content of the polymer being at least 50 mole percent, based on the polymer, and an α,β-ethylenically unsaturated mono-carboxylic acid, the acid monomer content of the polymer

being from 0.2 to 25 mole percent, based on the polymer, the monomer-carboxylic acid polymer containing uniformly distributed through the polymer a metal ion having a valence of 1 to 3 inclusive, and polymers of said olefin content and a α,β-ethylenically unsaturated dicarboxylic acid, the acid content of the polymer being from 0.2 to 25 mole percent based on the polymer, the dicarboxylic acid copolymer containing uniformly distributed throughout the polymer a mono-valent metal ion, in which at least 10 percent of the carboxylic acid groups of the monovalent and divalent carboxylic acid polymers are neutralized by the metal ions.

Other usable core layers in lieu of the above described ionomeric resin include polyethylene, polypropylene, ethylene-vinyl-acetate, ethylene-ethyl-acrylate, acrylonitrile-butadiene-styrene, and various formulated blends of the above, all the foregoing preferably being in thicknesses ranging from 0.25 mm to 1.3 mm (0.010 to 0.050 inches). Such materials in such thicknesses would normally be inadequate, either alone, or as laminated to cloth layers, for modern standards of box and toe counter usage in most modern applications, particularly military boot usage, but can be provided in improved and acceptable form in more applications by the present invention.

Preferably, the ionomeric core layer has a thickness of 0.25 mm to 1.3 mm (0.010 to 0.050 inches), and can be 1/2 to 2/3 of the thicknesses of such resin layers employed in the context of practical commercial use (0.64 mm (0.025 inches) and higher) of the invention recited in the said Beckwith patent. Similar reductions of thickness can be made in equivalent fashion when using the other core materials mentioned above.

Each cloth layer may comprise woven, nonwoven, spunbonded, spunlaced, stitchbonded, melt-bonded, chemically bonded and needled layers of cotton, rayon, nylon, poly-

ester, polypropylene and blends of the above. Weight ranges can be from 34 gm^{-2} to 270 gm^{-2} (1 oz yd^{-2} to 8 oz yd^{-2}). The impregnant may be polystyrene per se or may comprise copolymers of styrene with one or more other comonomers, for example butadienes, acrylonitrile and acrylates.

Styrene-butadiene, styrene-acrylonitrile, styrene-acrylate, acrylonitrile-butadiene, polyvinyl acetate and polyvinyl alcohol saturated fabrics are per se known as reinforcing materials for shoe counters and box toes. Preferably 100% polystyrene or a 90-10% (by weight) polystyrene-butadiene copolymer is employed. Polystyrene is activatable in aromatic solvents. Preferably one of toluene, methyl ethyl ketone, methylene chloride or 1,1,1-trichloroethane is utilized. The activation may be effected by surface coating the polystyrene with solvent or dipping the polystyrene layer (and any other layer laminated thereto) into the solvent. Heat activation may be used additionally or in lieu of solvent activation for polystyrene or other fabric saturants. As used herein, "heat activation" includes radiation as well as conductive, corrective, radiant and external heating and chemical internal heating.

The invention will now be further described by way of example only with reference to the drawing of which the single figure is a highly schematic cross-section through a reinforcing laminate embodying the present invention.

The laminate of the drawing comprises a core 10 of ionomeric resin as described above sandwiched between saturated fabric layers 12, each of which comprises a non-woven or woven fabric 14. The ionomeric resin layer is produced as described in U.S. Patent No. 3 264 272 to Rees and extruded as mentioned in the Beckwith patent. The fabric layers are applied in contact to the ionomeric resin layer to form an initial laminate. The

resulting assemblage is then passed through water-base latex styrene to form a final laminate. Optionally the final laminate product may be post calendared with a high pressure roller at room or elevated temperature.

There are exposed ends of the fabric 14 which lock into the ionomeric resin layer 10 and enhance bonding generally between the resin layer 10 and the fabric 14 and thus with layers 12. The laminate so produced can be rolled up for shipping, cut to desired shapes such as for counters, box toe blanks and the like and prepared for moulding by the user by solvent activating or heat activating the saturant of the saturated fabric layer, the application of solvent or heat being indicated by the arrows S/R. In the case of polystyrene saturant, the dipping of the laminate as a whole in aromatic solvents causes substantial softening of the saturant causing in turn particularly desirable moulding properties as well as adhesive properties. The cut-to-shape laminate portion as a whole can be heated and pressed in the moulding apparatus for further softening to enable moulding of the laminate as a whole to a desired shape and to effect adhesive bonding of the fabric layers 14 to a substrate layer SL and/or to an overlayer or cover layer OL via the impregnants. The steps of substrate and/or liner adhesive bonding can be made simultaneously with the moulding of the laminate or promptly thereafter in a separate step while the adhesive activity is high.

The resulting reinforcing element or reinforcing element/carrier combination (e.g., a military boot component) can afford a long, reliable service life with greater resistance to extreme conditions of weathering, oil exposure and heavy usage, particularly overcoming the problem of moisture vulnerability and impact resistance which has been a weakness of hitherto known products.

The solvent activation can be done at room temperature

and followed by a drying period that can be controlled to be fast or slow depending upon the solvent selected and the product density. The polystyrene/fabric layers exhibit high stiffness and adhesive properties while the necessary toughness in the context of such laminate usage is provided by the ionomeric resin core. The combination as a whole avoids the use of hot melt adhesives for bonding the reinforcement to a substrate, the bonding being effected substantially solely through the adhesive styrene, utilizes less styrene than in conventional styrene/fabric reinforcements, eliminates heat and moisture sensitivity through elimination of hot melt adhesives, allows use of less ionomeric resin or other resin than in conventional resin reinforcements and on the whole provides better bonding between integral parts of the reinforced (and optionally overlaid with a liner) substrate combination than in conventional combinations of such type and within the reinforcement, per se.

The combination further allows a faster shoe-making process because the toes are held firm by the plastic core while the activated styrene adhesive layer is "setting". This means that subsequent shoe-making steps can proceed more rapidly than with conventional styrene toes which must be allowed to age until firmness has developed.

CLAIMS:

1. A laminate comprising at least one layer of thermoplastic resin and at least one solvent- or heat-activatable adhesive impregnated cloth layer, the layers being bonded to each other at least in part through locking of cloth fibre portions of the cloth layer into the adjacent resin layer and the adhesive impregnant comprising a styrene saturant which is capable of impregnation into the cloth layer in liquid form and hardenable therein to form a stiff solid layer.

2. A laminate according to claim 1, in which the thermoplastic resin is an ionic copolymer of a monomer feed comprising at least 50 mole percent of an α-olefin having the general formula RCH = CH_2 where R is selected from the class consisting of hydrogen and 1 to 8 carbon atom alkyl radicals, 0.12 to 25 mole percent of an α,β-ethylenically unsaturated monocarboxylic acid and 0.2 to 25 mole percent of an α,β-ethylenically unsaturated dicarboxylic acid, the copolymers having at least a uniformly distributed 10 percent of the carboxylic acid groups of the mono- and di-carboxylic acids therein neutralized by metal ions of 1 to 3 valence.

3. A laminate according to claim 1 or claim 2, wherein the resin layer is sandwiched between two impregnated cloth layers bonded to the resin layer.

4. A laminate according to claim 1, 2 or 3 having a substrate layer adhesively bonded to an impregnated cloth layer substantially solely by the adhesive of the impregnated cloth layer.

5. A laminate according to claim 3, having respective substrate and cover layers adhesively bonded to the impregnated cloth layers substantially solely by the adhesive of the impregnated cloth layers.

6. A laminate according to any one of claims 1 to 5, wherein the resin layer has a thickness of 0.25 to 1.3 mm (0.010 to 0.050 inches).

7. A process of making a laminate, the process comprising extruding a thermoplastic resin to form a resin layer, adhering a cloth layer to the freshly-extruded resin layer and impregnating the cloth layer with a solvent- or heat-activatable adhesive comprising a styrene saturant which is capable of impregnation into the cloth layer in liquid form and hardenable therein to form a stiff layer.

8. A process according to claim 7, including activating the adhesive of the cloth layer and bonding by the activated adhesive a substrate layer to the cloth layer.

9. A process according to claim 8, in which the activation of the adhesive of the cloth layer and the bonding of the substrate layer are carried out simultaneously.

10. A process according to claim 7, 8 or 9 in which the adhesive is solvent activatable.

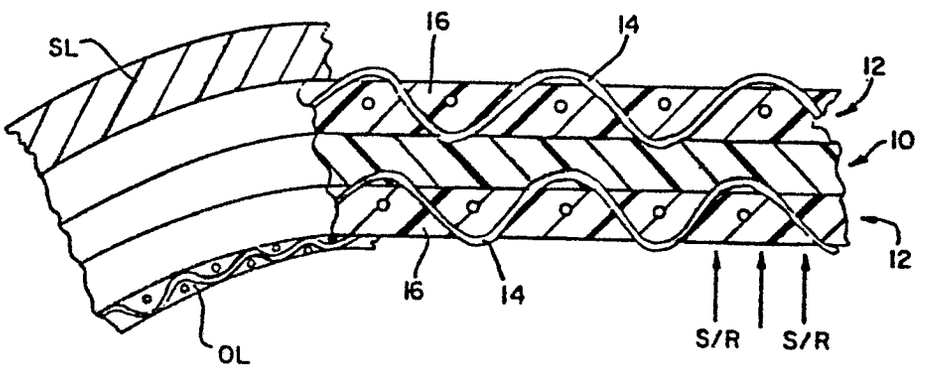
11. A process according to claim 10, including impregnating the cloth layer with a solvent-activatable adhesive, solvent-activating the adhesive and bonding the substrate layer to the cloth layer by the application of heat and pressure.

12. A process according to claim 10 or 11, in which the cloth layer is impregnated with polystyrene which is activated by aromatic solvent activation.

13. A process according to claim 12, in which the solvent is toluene, methyl ethyl ketone, methylene chloride or 1,1,1-trichloroethane.

14. A process according to any one of claims 8 to 13, in which the laminate is moulded to produce a shaped product comprising resin, cloth and substrate layers.

15. A process according to claim 14, in which the moulding is carried out simultaneously with the bonding of a substrate layer to the cloth layer.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EUROPEAN SEARCH REPORT

Application number

EP 82 30 4050

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
D,Y	US-A-3 427 733 (E.L.BECKWITH) *Claims 1-3; column 1, line 62 - column 2, line 29; column 3, line 1 - column 4, line 75; figure 1*	1-9,14,15	A 43 B 23/16 B 32 B 27/12
Y	GB-A-1 182 669 (FOSS MANUF.) *The whole document*	1,3,7,9,11,12	
A	DE-A-1 760 865 (RHEWOFLEX) *Claims 1,6; page 7, paragraph 2 - page 8, paragraph 1; examples 1,2*	8-12,14	
A	US-A-3 531 367 (R.KARSTEN) *Claim 1; column 2, lines 14-50; column 3, lines 23-68*	8-10,12,13	TECHNICAL FIELDS SEARCHED (Int. Cl. ³) B 32 B A 43 B
A	GB-A- 621 867 (SYLVANIA INDUSTRIAL) *Claims 1,2,6-8; page 1, line 96 - page 2, line 101; page 3, line 51 - page 4, line 22*	1,7,11	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	07-04-1983	BLASBAND I.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document